

REMOVAL OF TRU MICROQUANTITIES FROM RADIOACTIVELY CONTAMINATED SOILS IN LIQUID CO₂ MEDIUM

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SUMMARY

It is found that the solutions of tributylphosphate (TBP), di-2-ethylhexylphosphoric acid (D2EHPA) and octyl alcohol in liquid carbon dioxide allow removing 50-90 % of trivalent rare-earth and transplutonium elements from soil. As a result of 2-3-successive operations for soil decontamination by complexone solutions in liquid CO₂ it has been possible to increase the recovery of americium and rare-earth elements up to 90-99%. It is shown that the use of complexone solutions in liquid carbon dioxide enables to reduce the secondary liquid radwaste volume by a factor of more than 150 and to decrease the duration of treatment operation six times.

INTRODUCTION

One of the most important problems on rehabilitation of radiocontaminated territories is to remove the microquantities of the most ecologically hazardous long-lived transuranium elements (TRU) from soils. It is known that the solutions of hexafluoroacetylaceton (HFA) and tributylphosphate (TBP) [1,2] or the solutions of organophosphorus acids in supercritical carbon dioxide may be used for soil decontamination [3]. However, high pressure (~ 200 atm.) and high cost of equipment for supercritical fluid extraction are main disadvantages of this process.

The present work was aimed at demonstrating the feasibility of the compounds listed above in liquid carbon dioxide as applied to soil decontamination; the use of liquid carbon dioxide should make it possible to use less expensive equipment and to reduce working pressure to 60-70 atm.

EXPERIMENTAL PROCEDURE

Hexafluoroacetylacetone («Fluorochem», UK) was used without any additional purification. Tributylphosphate, octyl alcohol, pyridine, di-2-ethylhexylphosphoric acid and other reagents were received from "Vekton" Ltd (Russia) and were used without purification as well.

To conduct investigation on decontamination of soil in carbon dioxide medium, soil samples with different radionuclide-contamination degree were taken at "Mayak" PA site. The samples were taken from 0,1-0,2 m depth. Sample 1 is a soil-plant layer, samples 2 and 4 - clays with various content of sandy fraction, sample 3 - sand with residual plant roots. The taken soil samples were dried at 60 °C for 4 hours, screened through a 5 mm sieve to separate coarse fragments and were analyzed for radionuclide content. Results of γ -spectrometric analysis are presented in Table 1.

Table 1 Radionuclide content in soil samples

?	Sample description	Sample activity, Bq/g				
		Am ²⁴¹	Eu ¹⁵⁵	Eu ¹⁵⁴	Ce ¹⁴⁴	Pu ²³⁹
1.	Soil-plant layer	1060	190	600	80	630
2.	Clay	160	82	28	59	147
3.	Sand	530000	160	80	50	73
4.	Loam	220	113	412	210	68

For experiments a high-pressure syringe pump with cooled head (Grant-Instrument, Russia), and stainless-steel extraction cells (3,5 ml, Keystone Scientific, USA) covered with pyrolytic chrome were used. Soils were decontaminated in liquid CO_2 at 70 °C and 25 MPa. To do this, into the first cell - bubbler - complexones were poured, into the second one a weighed soil portion was placed (3,0 g). Carbon dioxide was supplied by syringe pump into bubbler, where CO_2 was saturated with complexones and next passed into the second extraction cell. Time of static extraction was 40 min, that of subsequent dynamic extraction - about 200 min. During dynamic extraction 100 ml CO_2 at flowrate 0,5 ml/min were pumped through both cells. Thus, the total duration of the experiment was 4 hours. Extract was collected into methyl alcohol through a capillary. In some cases, upon a single treatment operation, new portions of complexones were poured into bubbler and the operation was repeated according to the procedure described above.

Plutonium was recovered from soil by aqueous solutions in accordance with the procedures similar to those described in [4,5]. A weighed soil portion (3 g) was placed into glass flask wherein 50 ml of 0.5 M/g HNO_3 solution were poured. Leach-out process was conducted on periodical stirring for 24 hours. Then the solution was separated from soil by filtration and soil was poured with fresh solution portion. Radionuclide content was determined in all products by α -spectrometry.

RESULTS AND DISCUSSION

At the first investigation stage the effect of modifiers - pyridine (Py) or tributylphosphate (TBP) - on radionuclide removal degree by HFA solution in liquid carbon dioxide was compared. The investigation showed that both modifiers enable efficiently to remove transplutonium and rare-earth elements from different soils (Table 2). Depending on soil type, 50-90 % of trivalent rare-earth and transplutonium elements may be removed in a single operation. At the same time the operations of efficient removal of plutonium failed. Two-and three-fold treatment of soil under these conditions allows recovering up to 99% of americium and rare-earth elements, but only slightly affects the degree of plutonium removal.

As HFA is a rather expensive extractant, we attempted to do away with its use. Most radionuclides are present in soil in the form of oxides or basic salts and it is evident that the main role of HFA is the formation of hydrophobic complexes with radionuclides. Thus, D2EHPA may be used instead of HFA. Experimental data are given in Table 3.

The conducted experiments have shown that the recovery degree of plutonium, americium and rare-earth elements does not practically differ from decontamination by HFA solutions in liquid carbon dioxide. By this is meant that the cheap commercial reagents may be used instead of expensive HFA.

Table 2 Removal of radionuclides from soil by treatment with HFA solutions in liquid CO_2 , containing water and modifier (3 g soil, 0,2 ml HFA, 0,2 ml CO_2 , 70 °C, 25 °P)

Sample number	Modifier, ml		Radionuclide content in soil after treatment, %				
	Py	TBP	Am ²⁴¹	Eu ¹⁵⁵	Eu ¹⁵⁴	Ce ¹⁴⁴	Pu ²³⁹
? 1 - Soil-plant layer	0,2	---	45	67	80	20	82
	---	0,1	50	35	30	35	80
? 2 - Clay	0,2	---	27	59	18	45	83
	---	0,1	33	46	28	43	85
? 3 - Sand	0,2	---	53	69	73	47	79
	---	0,1	42	27	49	73	80
? 4 - Loam	0,2	---	13	25	12	8	72
	---	0,1	17	21	18	4	73

Table 3 Radionuclide removal from soil by solutions of TBP, D2EHPA and octanol in liquid carbon dioxide in the presence of water (3 g soil, 0,1 ml TBP, 0,2 octanol, 0,2 ml CO_2 , 70 °C, 25 °P)

? soil	Operation number	Radionuclide content in soil after treatment, % of initial				
		Am ²⁴¹	Eu ¹⁵⁵	Eu ¹⁵⁴	Ce ¹⁴⁴	Pu ²³⁹
? 1 - Soil-plant layer	1	10	25	25	?.?.	74
	2	7	20	18	?.?.	67
	3	6	15	16	?.?.	62
? 2 - Clay	1	17	37	53	62	86
	2	9	25	29	31	78
	3	1	12	18	21	73
? 3 - Sand	1	33	25	42	59	82
	2	26	13	27	35	75
	3	21	9	24	31	74
? 4 - Loam	1	23	32	26	?.?.	64
	2	11	26	23	?.?.	59
	3	10	24	22	?.?.	57

n.d. - not detected, radionuclide content below 0.5 Bq/g

At the close of the investigation a comparison was carried out between soil decontamination efficiency with the use of complexone solutions in liquid carbon dioxide and aqueous solutions of nitric acid. The data given in Table 4 indicate that all soluble forms of plutonium being removed on soil decontamination by traditional techniques are also removed to the same degree by complexone solutions in liquid carbon dioxide.

It should be noted that it has taken 150 ml of 0.5 M HNO₃ and 72 hours to remove the soluble forms of plutonium (37-38 % of total Pu content) from 3 g of soil-plant layer by traditional techniques. Similar results were attained within 12 hours for soil decontamination in liquid carbon dioxide by using less than 2 ml of TBP-D2EHPA-octanol mixture and 0.6 ml H₂O. Hence, the decontamination process in carbon dioxide enables to reduce the secondary liquid waste volume by a factor of more than 150 and to decrease the duration of decontaminating treatment six times.

Table 4 Comparison of plutonium leaching degree from soil-plant layer by aqueous solution of nitric acid and complexone solutions in liquid carbon dioxide

Treatment operation number	Plutonium content in soil after treatment, % of initial	
	Aqueous solution 0.5 M HNO ₃ 50 ml, 24 h	Solution 0,2 ml TBP, 0,2 ml D2EHPA, 0,2 ml octanol and 0,2 ml water in 100 ml ? ? ₂ (70 ?tm.), 4 h
1	78	74
2	68	67
3	63	62

CONCLUSION

The investigation has shown that the solutions of hexafluoroacetylacetone in liquid carbon dioxide in the presence of a modifier (pyridine or tributylphosphate) allows to remove 50 - 90 % of trivalent rare-earth and transplutonium elements and only about 20 % of plutonium from soil. 2-3-successive operations of soil decontamination by HFA - TBP or HFA - Py solutions enable to increase recovery of americium and rare-earth elements up to 90-99%, but plutonium recovery increases only to 30%. The nature of modifier does not practically affect the radionuclide recovery degree.

It is found that the replacement of expensive HFA with D2EHPA - octanol mixture has no influence on the recovery degree of plutonium, americium and rare-earth elements from soil in liquid carbon dioxide medium. Thus, the cheap commercial reagents may be used instead of expensive HFA.

The performed experiments have confirmed that the use of complexone solutions in liquid carbon dioxide makes it possible to reduce the secondary liquid radwaste volume by a factor of more than 150 and decrease the duration of decontaminating operations six times as compared to traditional decontamination techniques.

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REFERENCES

- [1]. B.J. Mincher, R.V. Fox, R.G.G. Holmes et al., *Radiochim. Acta*, 2001, 89, p. 613-618
- [2]. A. Shadrin, A. Murzin, V. Romanovsky et al., 5th Meeting on Supercritical Fluids, 23-25 March 1998, Nice, France, 1998, Proceedings, 155-160
- [3]. A. Shadrin, A. Murzin, V. Starchenko et al., *Spectrum'98*, Denver, Colorado, USA, September 13-18, 1998, Proceedings, American Nuclear Society Inc, USA, 1998, p. 94-98
- [4]. F.I. Pavlotskaya, *Migration of global radioactive fallout products in soil*, M., ? tomizdat, 1974, p. 215.
- [5]. V.M. Prokhorov, *Migration of radioactive contaminants in soil*, M., Energoizdat, 1981, p. 99.